

Full Paper

Prediction and Comparison of Shelf Life of Solid Rocket Propellants Using Arrhenius and Berthelot Equations

Himanshu Shekhar*

High Energy Materials Research Laboratory, Sutarwadi, Pune 411 201 (India)
e-mail: himanshudrdo@rediffmail.com

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Abstract

The Arrhenius equation and the Berthelot equation for the prediction of shelf life of composite propellant formulations are compared. The elongation has a measurable variation with time and is taken as the fastest degrading parameter for HTPB/AP/Al based composite solid rocket propellants. An HTPB based aluminized composite propellant with 85% solid loading and an initial elongation of 63.24% is prepared. It is kept at an elevated temperature of 60°C to achieve a higher rate of degradation for a prolonged time period (1 year). The elongation is monitored at regular intervals using JANNAF class C dog bone specimen in uni-axial tensile mode. A reduction of the elongation to less than 50% is taken as the end-of-shelf life of the propellant. The shelf life of the propellant is calculated to be 1.2 years at 60°C. For the extrapolation of the shelf life at 60°C to the shelf life at 27°C, the results of both the Arrhenius equation and the Berthelot equation are compared. The activation energy (E) in the Arrhenius equation is obtained as 72.8 kJ mol⁻¹ and the 10°C reaction rate rise factor (γ_{10}) is found to be 2.4. This comparison is independent of the propellant formulation and other researchers have reported a similar range of values for these parameters. The shelf life of this propellant formulation at 27°C is conservatively predicted to be 20 years using both equations. In addition to estimation of shelf life by both equations using elongation as control parameter, this paper gives scaling curves, which are valid universally for predicting shelf life at 27°C from data of shelf life at 60°C. The use of scaling curves is independent of properties, propellant formulation and degradation mechanism considered for analysis.

Keywords: Activation Energy, Arrhenius Equation, Berthelot Equation, Composite Propellant, Elongation, Shelf Life

1 Introduction

Solid rocket propellants are the source of power for the propulsion of rockets, missiles and launch vehicles. Many a time, the performance of a system deteriorates with

time due to thermal, environmental, chemical, physical and internal changes. Propellants being highly filled polymers are prone to deteriorate before the malfunction of any other electronic or hardware components in complete propulsion systems. So, the shelf life of the complete system is governed by the shelf life of the propellants used in the system. Since the shelf life of propellants is restricted by several co-occurring, competing and simultaneous mechanisms, it is difficult to ascertain the correct mechanism. One exhaustive, time-consuming method to predict shelf life is the surveillance of complete systems under normal storage conditions for a prolonged time period and the measurement of a performance parameter regularly to ascertain their actual shelf life. However, most of the literature advocates the use of accelerated aging of propellants at elevated temperatures and then predicting shelf life at that elevated storage temperature. From the shelf life at elevated temperature, the shelf-life at normal storage conditions is calculated by either Arrhenius equation or Berthelot equation. The present paper assesses both methods for the prediction of shelf life in order to streamline the prediction methodology.

2 Shelf-Life Prediction Methods

Although propellant degrades due to stabilizer migration, oxidation, rise in cross-linking density, thermal or radiation damages, environmental effects, etc., the fastest reaction rate parameters should be selected for assessment of shelf-life. The parameter may be mass loss on heating, vacuum stability, auto ignition, thermal stability, mechanical properties degradation, change in ballistic performance [1], etc. In addition, these parameters should undergo measurable change during ageing or storage. The criteria for assessing end of shelf life should be well de-

fined beforehand. However, shelf life prediction mechanism using accelerated ageing data mainly needs scaling up of shelf life from elevated temperature to that at reference temperature. Two equations are mostly used for such correlations.

Arrhenius equation is more popular method and is mainly depicting an exponential correlation for reaction rate constant of chemical reactions [2,3]. The Arrhenius equation is given by Eq. (1).

$$k = A \times e^{-\frac{E}{RT}} \quad (1)$$

where k is reaction rate, A is pre-exponential factor, E is activation energy (kJ mol^{-1}), R is the universal gas constant ($\text{J mol}^{-1} \text{K}^{-1}$), and T is absolute temperature (K).

Since the activation energy, if expressed in J mol^{-1} , is numerically high with trailing zeros, generally kJ mol^{-1} is used to represent the activation energy [4,5]. The reaction rate (k) is defined as the change of a property per unit time. If similar degradation of a property at two temperatures is considered, the reaction rate is proportional to the shelf life at the two temperatures. The pre-exponential factor (A) is a valuable parameter in the Arrhenius equation but it gets eliminated, when the reaction rates at two temperatures are considered. The activation energy (E) is an important parameter in the Arrhenius equation and is generally treated as a constant for the given temperature range. If various parameters at two different temperatures T_1 and T_2 are represented by subscripts 1 and 2, respectively, the correlation of shelf lives at two temperatures is given by Eq. (2). Researchers also depict this as relative reaction rate (RRR) [6].

$$\text{Ln}\left(\frac{t_2}{t_1}\right) = -\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (2)$$

where t_2 is shelf life at temperature T_2 , t_1 is shelf life at temperature T_1 .

Although this is a very popular method, researchers [7] criticize this correlation. Main objections are the validity of Arrhenius equation for isothermal ageing only, the non-linear relation between the measurable properties and the ageing time at high temperatures, the neglect of other ageing mechanisms, dependence of the reaction rate constant on time, etc. It is also reported to give higher predicted shelf life [8]. As clear from Eq. (2), log of time-period is inversely proportional to temperature.

The Berthelot equation is another approach to predict shelf life of propellants. In this case, log of time to base 10 is directly proportional to temperature. The main assumption of this method is that for same difference in temperature, the reaction rate changes by the same amount. Generally 10°C is taken as a standard and for every 10°C rise or fall in temperature, the propellant properties changes by the same fraction, defined by γ_{10} . The shelf life prediction correlation is given as Eq. (3).

$$\frac{t_2}{t_1} = (\gamma_{10})^{\frac{T_1 - T_2}{10}} \quad (3)$$

Equation (3) is also called Van'T Hoff rule and it can be derived from Berthelot equation readily. Several values of γ_{10} are reported in the literature. For double base propellants, a value of γ_{10} of 1.8 is generally taken, if the temperature difference is considered in Fahrenheit [9]. This becomes 2.88, if the change in temperature is considered in degree Celsius. Other researchers also reported similar values (around 3) for double base propellants [10,11]. For composite propellants, no such value is available. To assess and compare results, an HTPB based aluminized composite propellant is aged at an elevated temperature of 60°C for a long time period till the propellant degraded as per pre-decided criteria.

3 Experimental Results

A solid propellant formulation containing 67% oxidizer (ammonium perchlorate), 15% metallic fuel (aluminum) and 14% binder (HTPB: hydroxyl terminated polybutadiene 11% and DOA: di-octyl adipate 4%) is prepared by vacuum casting. Cross-linking agent, process aids, and burn rate modifiers are added in small percentage (less than 0.5%) to meet the ballistic requirements. The cast propellant composition is cured using toluene diisocyanate (TDI) at 50°C for 5 d.

For study of ageing and determination of shelf life, mechanical properties data are considered to be convenient, representative and measurable. The propellant is kept at 60°C in an oven, where the temperature is maintained by the circulation of dry air with a relative humidity less than 20%. At regular intervals, samples are drawn and tested for mechanical properties. The elongation is monitored in uni-axial tensile tests at a testing speed of 50 mm min^{-1} for JANNAF Class C dog bone specimen at regular intervals of time. Grip distance and gauge lengths are taken 68 mm. Initial value of percentage elongation is 63.24%. The degradation criterion is defined as a reduction of the elongation to less than 50%. Propellant specimens are tested at regular intervals till the elongation reduces to less than 50%. The monitored values of elongation are reproduced in Figure 1.

Exponential, logarithmic, second order polynomial and power law variations are fitted to the measured variation of elongation with time. Best-fit curve is obtained for logarithmic plot with highest correlation coefficient. The governing equation is given as Eq. (4) with correlation coefficient of 0.8514.

$$\varepsilon = -2.592 \times \text{Ln}(t) + 65.768 \quad (4)$$

where ε is elongation (%) and t is time (days).

From this relation, the time for degradation down to 50% elongation is calculated to be 438.39 d (1.2 years). This is the shelf life of the propellant formulation at a

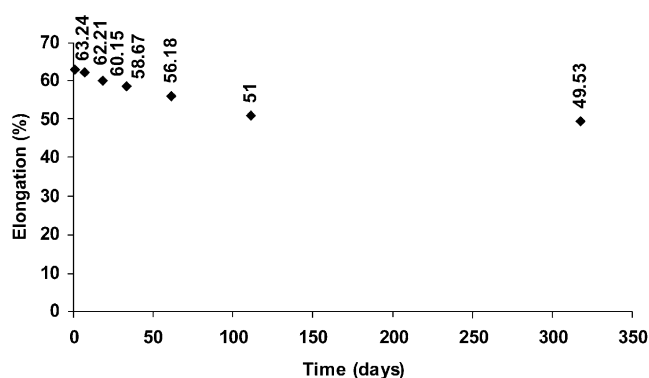


Figure 1. Variation of elongation with time.

storage temperature of 60°C. The prediction of shelf life at ambient temperature of 27°C is carried out by both Arrhenius equation and Berthelot equation.

4 Analysis and Discussion

Since the activation energy (E) of the Arrhenius equation and the change in the reaction rate due to every 10°C rise in temperature (γ_{10}) of the Berthelot equation are not known for the available composition and the measured parameter, different values of E and γ_{10} are taken to compare the scaling factor (ratio of shelf lives at two temperatures). The scaling factor is the ratio of the shelf life of a propellant due to storage at 27°C to that at 60°C. A graph is plotted between scaling factor and value of these parameters (Figure 2).

The value of the activation energy is varied from 10 to 140 kJ mol⁻¹ and the scaling factor is obtained. It is clear that a higher value of the activation energy leads to a higher value of the scaling factor. For example, for $E = 50$ kJ mol⁻¹, the shelf life at 27°C is predicted as 8.73 years, which becomes 63.57 years for an activation energy of 100 kJ mol⁻¹. Since different mechanisms of degradation have different activation energies, one unique value for the degradation cannot be assigned for the propellant formulation. The actual activation energy for the degra-

dation of the elongation of the given propellant formulation is to be ascertained. However, a lower value of the activation energy means, the degradation mechanism is diffusion controlled, while a higher value indicates kinetics controlled. The activation energy for propellant ageing is generally about 70 kJ mol⁻¹ and the value of shelf life of the propellant composition under study is around 19.32 years. Several values of shelf life of propellants are plotted against the activation energy as Figure 3.

The value of γ_{10} is varied around 3 and the scaling factor is plotted as shown in Figure 2. It is clear that a higher value of this factor leads to a higher value of the scaling factor and thereby a higher shelf life at 27°C. For $\gamma_{10} = 3$, the scaling factor is 37.54, which gives a shelf life of 45.08 years (37.45×1.2 years) at 27°C. Predicted shelf life by using Berthelot equation for different values of γ_{10} is plotted as Figure 4.

It is clear from Figures 3 and 4 that for the prediction of the same shelf life, the relevant parameters of both the Arrhenius and the Berthelot equations can be compared. For example a 10°C reaction rate rise factor (γ_{10}) of 2.1 in the Berthelot equation predicts a shelf life of 13.9, which approximately corresponds to an activation energy of 61.68 kJ mol⁻¹ from the Arrhenius equation. To elucidate the correspondence between the parameters the activation energy is plotted against the scaling factor for the same shelf life in Figure 5.

However, the same procedure can also be applied to data available from literature. Sammour [8] has predicted

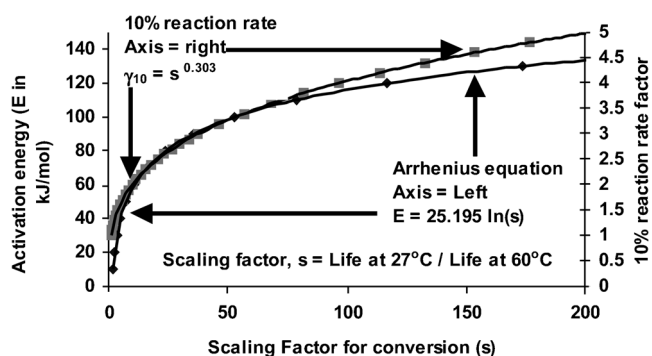


Figure 2. Comparison of main parameters of Arrhenius and Berthelot equation.

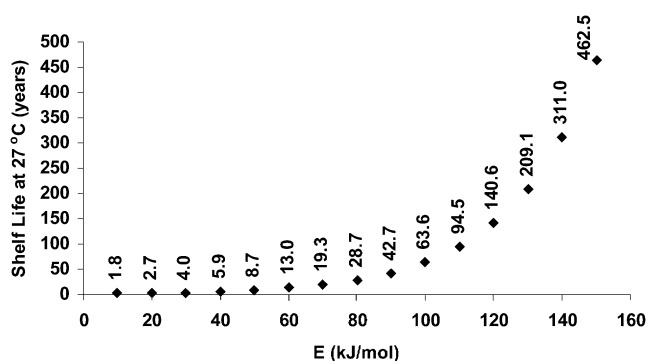


Figure 3. Predicted shelf life using Arrhenius equation.

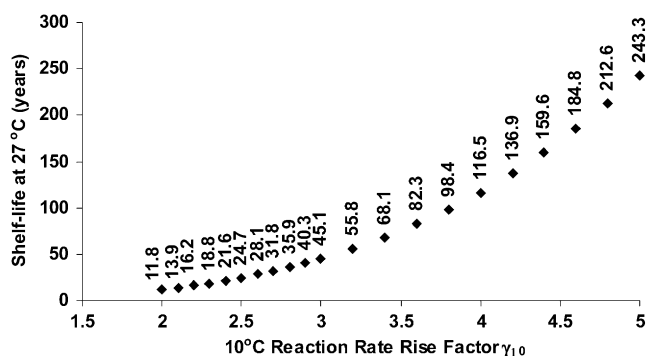


Figure 4. Predicted shelf life using Berthelot equation.

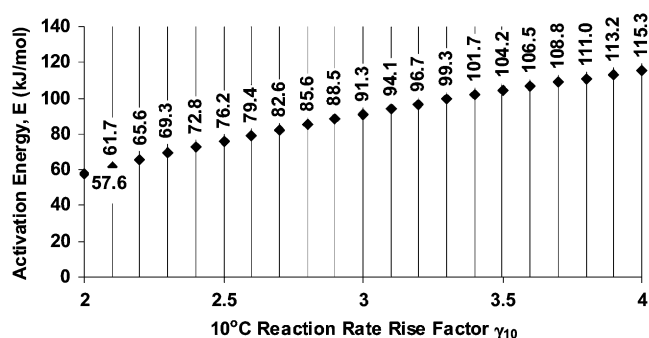


Figure 5. Comparison of Arrhenius and Berthelot parameters.

5 years of shelf life at 27 °C for cast double base (CDB) propellant from accelerated ageing test. The shelf life at 65.5 °C storage is obtained as 60 d. This corresponds to an activation energy of 74.96 kJ mol⁻¹ and 10 °C reaction rate rise factor of 2.43. Similarly for composite propellants, Judge [1] derived 9 weeks of shelf life at 70 °C which is equivalent to 983 weeks of shelf life at 20 °C. This gives a reaction rate rise factor of 2.56 and an activation energy of 78.51 kJ mol⁻¹. With an activation energy of 72.8 kJ mol⁻¹ or 10 °C reaction rate rise factor of 2.4, a shelf life of studied propellant formulation is calculated to be slightly more than 20 years at 27 °C. So on conservative estimates, the shelf life of the propellant formulation assigned as 20 years. The values of the parameters are in line with reported values and the predicted shelf life matches well with nominal shelf life of composite propellants.

5 Conclusion

Arrhenius equation and Berthelot equation for the prediction of the shelf life of composite propellants are compared. The Arrhenius equation has exponential variation of shelf life but Berthelot equation has power-law variation. Arrhenius equation depends on activation energy (E), while Berthelot equation is governed by 10 °C reaction rate rise parameter (γ_{10}). A correlation is obtained between these two parameters to predict the same shelf life at 27 °C. A composite propellant formulation with an initial elongation of 63.24 % is conditioned at 60 °C for prolonged time period and the time for the degradation of the elongation to 50 % is calculated to be 1.2 years by logarithmic best-fit curve. For the variation of the elongation with time for the composite propellant, an activation energy of 72.8 kJ mol⁻¹ or a 10 °C reaction rate rise factor of 2.4 gave a conservative shelf life estimate of 20 years. This is in line with reported values.

It must be noted that for different degradation mechanisms, different values of activation energy and 10 °C reaction rate rise parameter exists. For the degradation of the elongation of composite propellants based on HTPB/AP/Al, 72.8 kJ mol⁻¹ as activation energy and 2.4 as γ_{10} is valid, justified and experimentally demonstrated. The given scaling factor curves are independent of the composition and can be utilized for the prediction of shelf life at 27 °C from shelf life at 60 °C.

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